

# U L<sub>3</sub>-edge XAFS at environmentally relevant concentrations

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## Outline

- U concentrations
- Introduction U-Ca-CO<sub>3</sub>
- Experimental feasibility
- Data and Models
- Conclusions



# Environmentally relevant U concentrations

- EPA limit in ground water  $30\mu\text{g/L} \sim 0.1\mu\text{M}$
- Field Research Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee  $\sim 70\mu\text{M}$
- Uranium Tailings Remedial Action (UMTRA) Tuba City, AZ  $\sim 2\mu\text{M}$
- Palmotto U deposit, Finland  $\sim 1\mu\text{M}$
- Other considerations
  - APS limit for  $[\text{U}]/\text{sample} < 50 \mu\text{g}$
  - Using a small sample  $3.3 \times 10^{-4} \text{ Liters} \sim 600\mu\text{M}$



# Bioremediation of U(VI)

- Activities associated with mining and processing of U ores have resulted in vast areas of contamination.
- Dissimilatory metal reducing bacteria (DMRB) couple the oxidation of organic matter or H<sub>2</sub> to the reduction of oxidized metals including U(VI).
- U(IV) is less mobile and has lower solubility than U(VI).
- Rapid rate of microbial reduction of U(VI) makes bioremediations an attractive option for removing U from contaminated groundwaters.
- Factors that enhance or inhibit bacterial U(VI) reduction are not well understood.

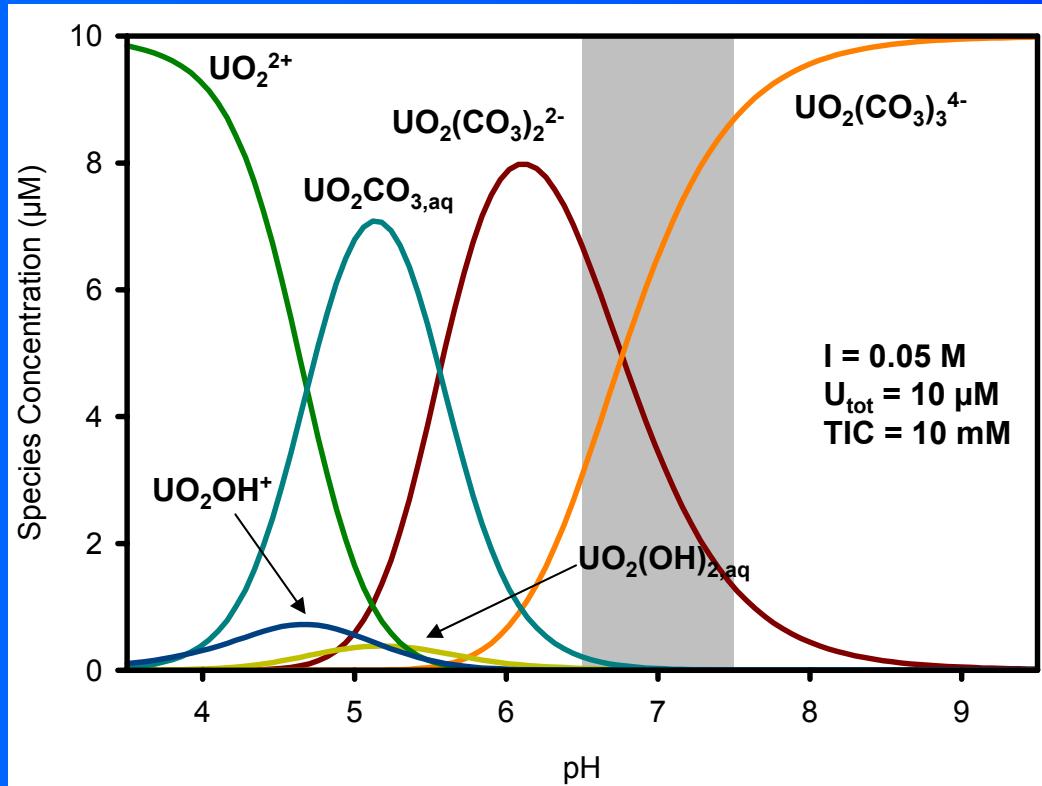


# Factors effecting bioreduction of U(VI)

- Multidentate organic ligands
  - R. Ganesh *et. al.* Appl. Environ. Microbiol. 1997, 63 4385.
- Bicarbonate
  - Phillips, E.J.P., *et. al.* J. Ind. Microbiol. 1995, 14, 203.
- Nitrate or sulfate
  - K.G. Robinson *et. al.*, Water Environment Federation, Chicago, IL 1994, 199.
- Competitive electron acceptors, such as Fe(III)
  - B.E. Wielinga *et. al.* Environ. Sci. Technol. 2000, 34, 2190.
- Geochemical oxidants, such as Mn(IV) and Fe(III) oxides
  - C. Liu *et. al.* Environ. Sci. Technol, 2002, 36, 1452.
  - J.K. Fredrickson *et al.*, Geochim. Cosmochim. Acta, in press.

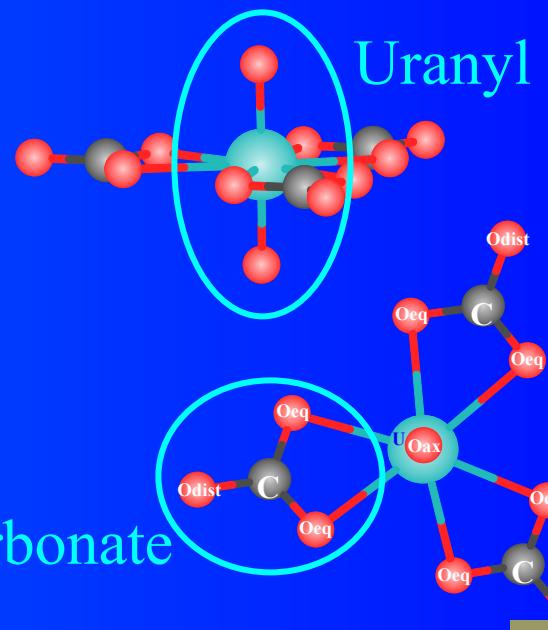


# Carbonate complexes play an important role in the aqueous speciation of uranyl ion.



Bidentate Carbonate

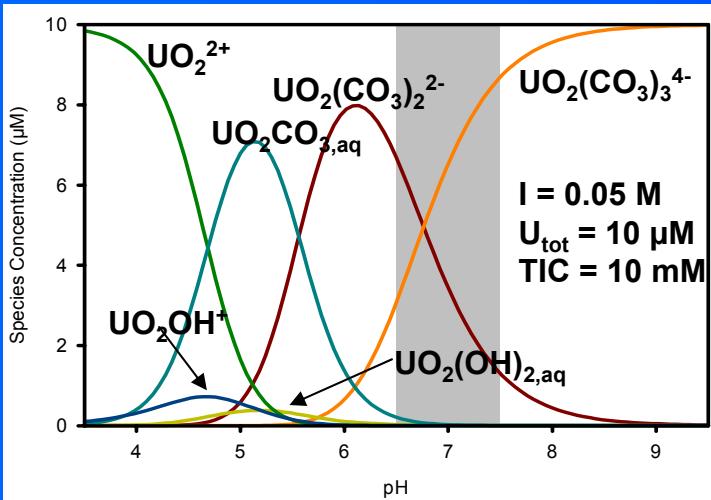
U(VI) aqueous speciation sensitive to pH in the range of many bioreduction experiments.



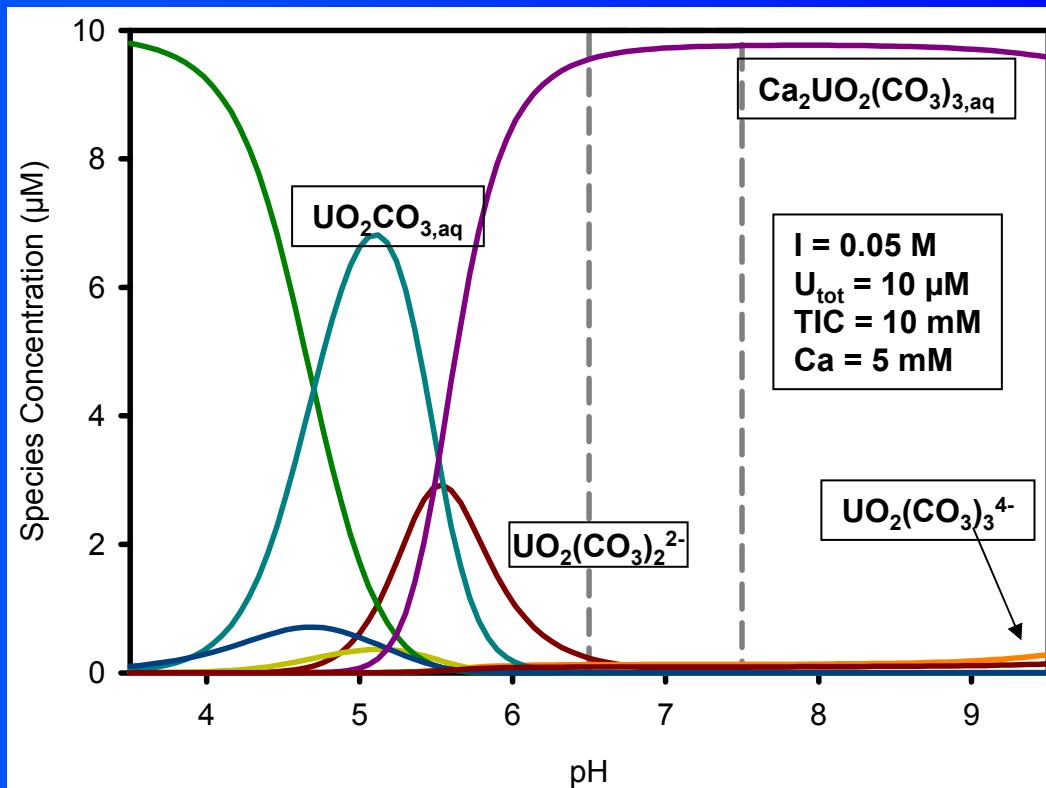
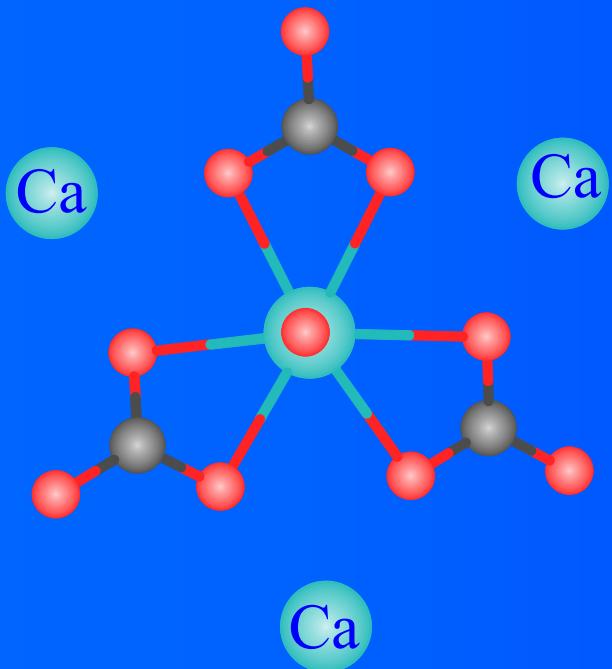
# Aqueous Ca-U(VI)-CO<sub>3</sub> complexes have recently been described in the literature:

- Bernhard et al., 1996; 2001.
- Kalmykov and Choppin, 2000.
- Reported formation constants suggest these complexes may be important in uranyl aqueous speciation ( $\log \beta_{113} = 25.4$ ;  $\log \beta_{213} = 30.55$ ).

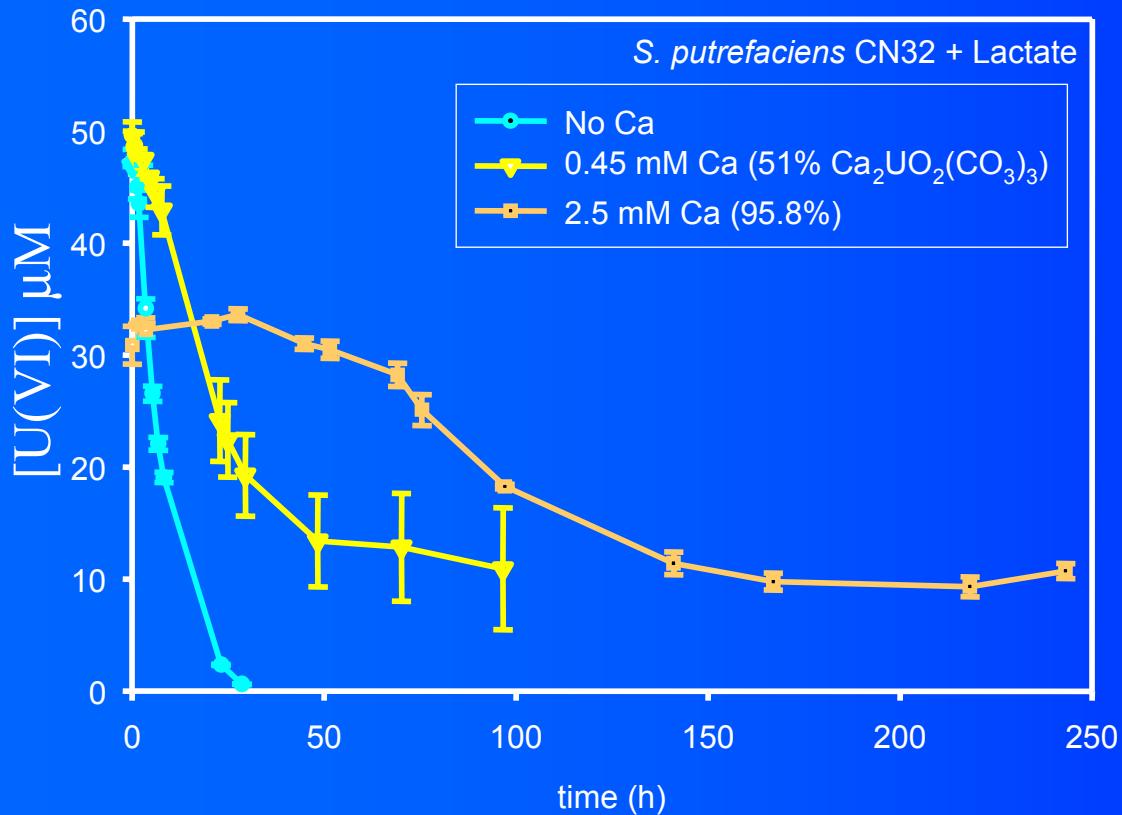




Consideration of the Ca-UO<sub>2</sub>-CO<sub>3</sub> complex results in a major shift in species distribution at pH > 5.



# Aerobically Cultured *Shewanella putrefaciens* CN32 Shows Decreased Rate of U(VI) Reduction in Presence of Ca.



- Other culture conditions:
  - 30 mM NaHCO<sub>3</sub>
  - 20% CO<sub>2(g)</sub>
  - pH 6.9
- In presence of Ca:
  - Lag phase to onset loss U(VI).
  - Incomplete reduction.

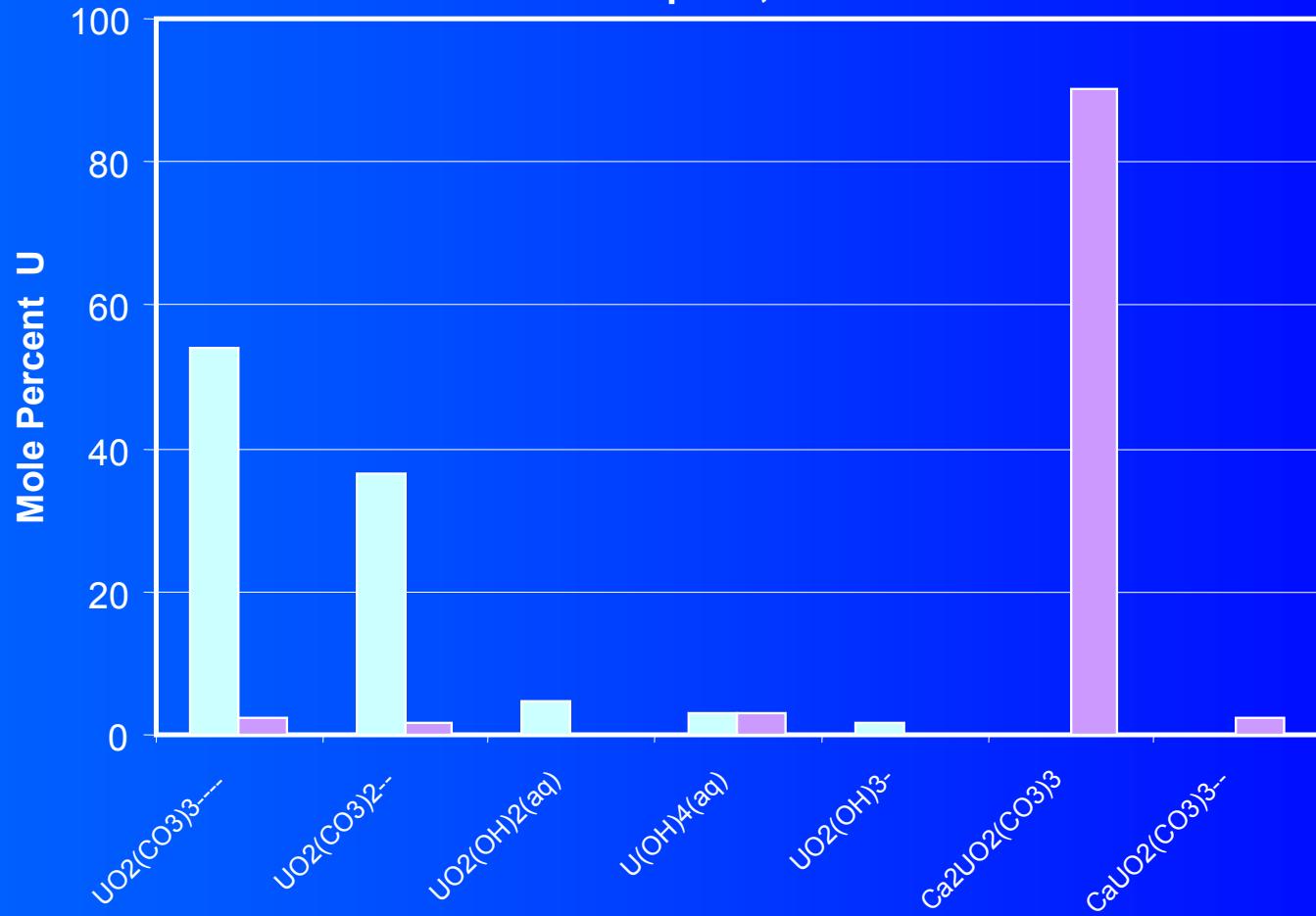
S.C. Brooks, J.K. Fredrickson, S.L. Carroll, D.W. Kennedy, J.M. Zachara, A.E. Plymale, S. Fendorf, K.M. Kemner, and S.D. Kelly, "Inhibition of Bacterial U(VI) Reduction by Calcium," *Environmental Science and Technology*, 2003, 37, 1850-1858



# Predicted Uranyl Species in Natural environments:

Palmetto U Deposit, Finland

	mM
Na <sup>+</sup>	0.97
Ca <sup>2+</sup>	0.45
Mg <sup>2+</sup>	0.18
K <sup>+</sup>	0.03
U(VI)	0.69 μM
U(IV)	0.022 μM
SO <sub>4</sub> <sup>2-</sup>	0.31
F <sup>-</sup>	0.019
HCO <sub>3</sub> <sup>-</sup>	1.4
Cl <sup>-</sup>	0.18
SiO <sub>2(aq)</sub>	0.16
pH	8.42



Results using standard data base

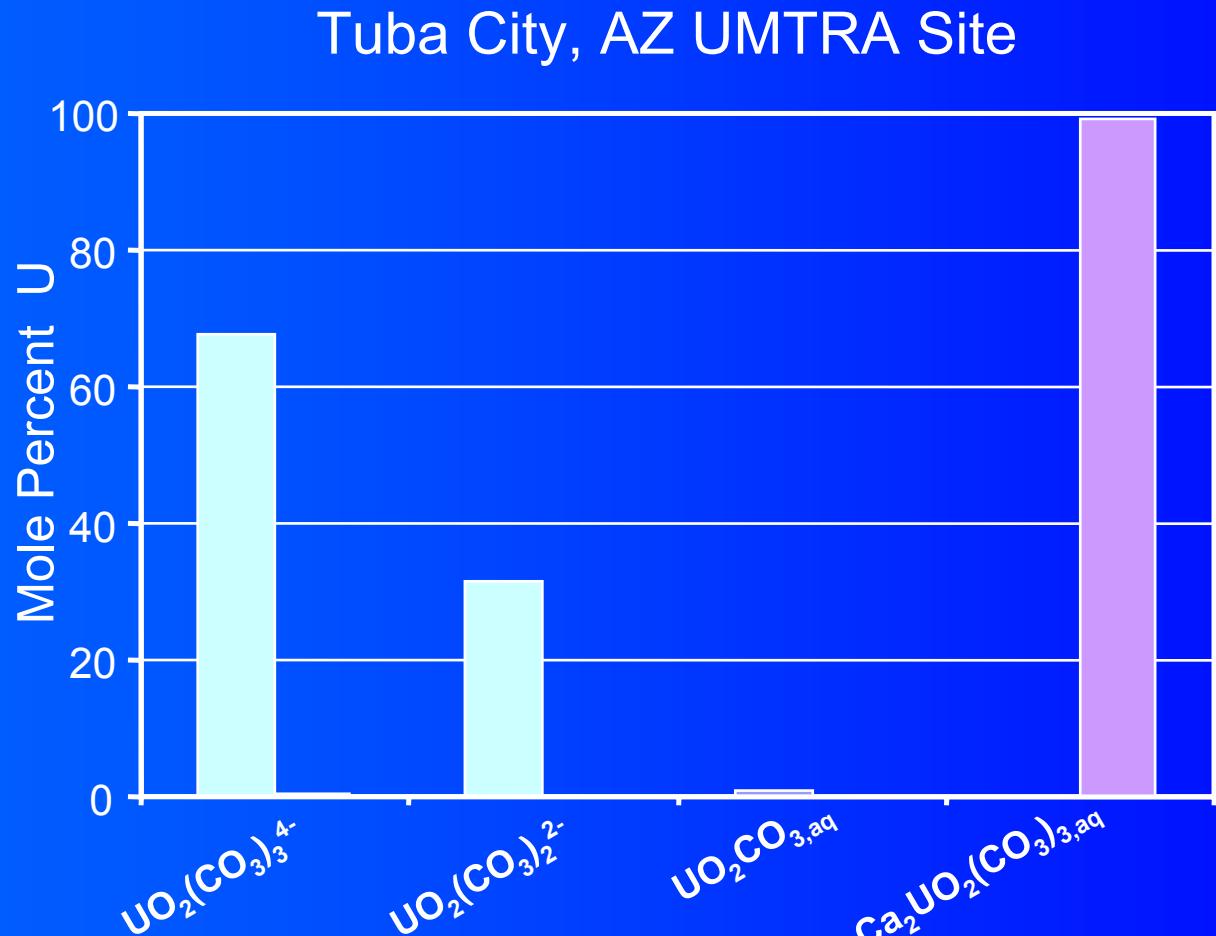
Results including formation constant for Ca-UO<sub>2</sub>-CO<sub>3</sub>



# Predicted Uranyl Species at Contaminated sites : UMTRA

	mM
Na <sup>+</sup>	27.2
Ca <sup>2+</sup>	19.7
Mg <sup>2+</sup>	14.7
K <sup>+</sup>	0.242
Sr <sup>2+</sup>	0.091
U	2.33 µM
SO <sub>4</sub> <sup>2-</sup>	24.7
NO <sub>3</sub> <sup>-</sup>	21.3
HCO <sub>3</sub> <sup>-</sup>	16.6
Cl <sup>-</sup>	14.9
HPO <sub>4</sub> <sup>2-</sup>	3.25 µM
pH	6.5
TDS	6820
T	16.3°C

\* Abdelouas et al., 1998



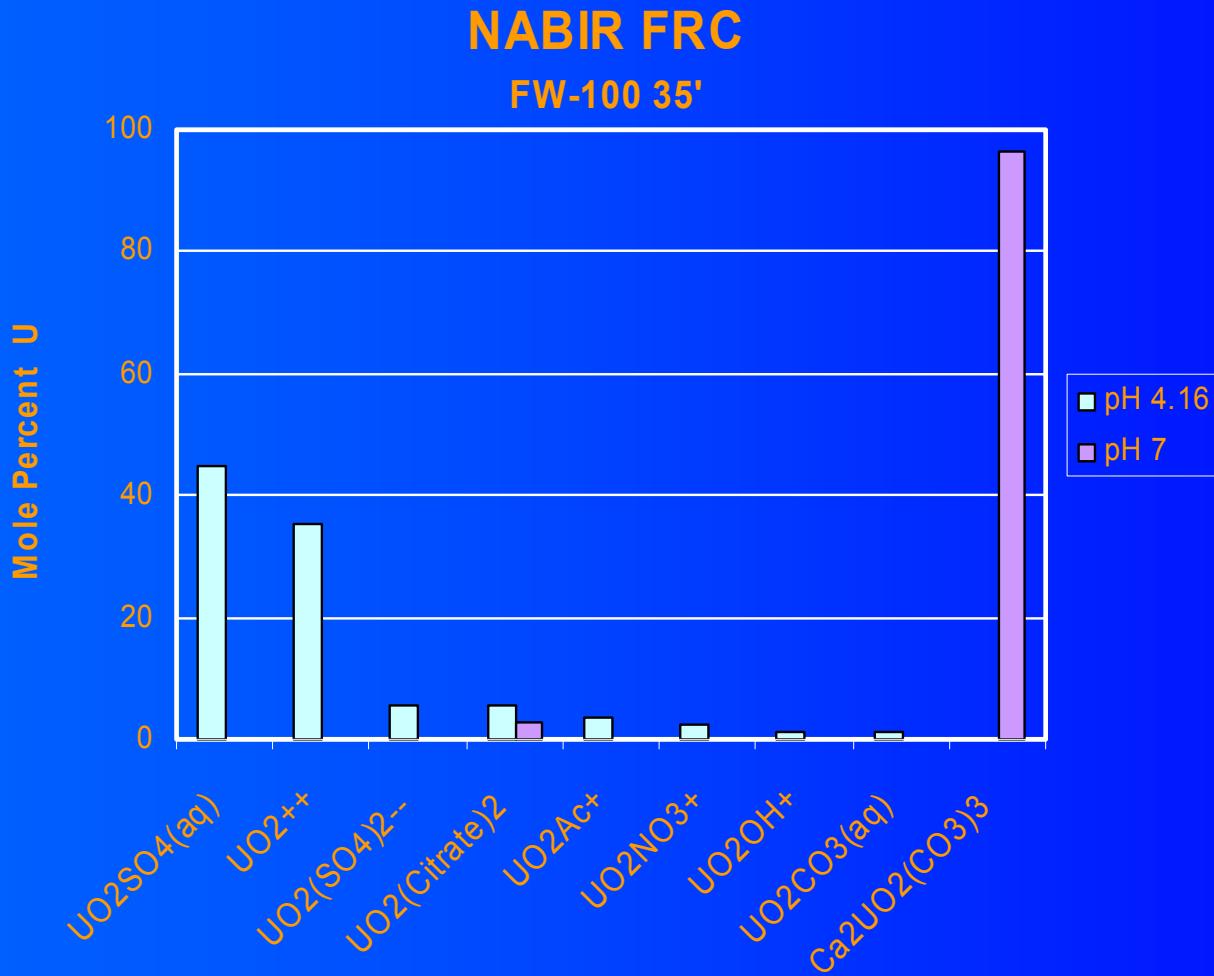
Results using standard data base

Results including formation constant for Ca-UO<sub>2</sub>-CO<sub>3</sub>



# Predicted Uranyl Species at Contaminated sites : FRC

	mM
Ca	38.9
Na	30.5
Mg	10.6
Al	6.78
Mn	1.74
K	1.45
Fe	0.35
$\text{NO}_3^-$	136.5
$\text{SO}_4^{2-}$	23.8
$\text{HCO}_3^-$	6.01
$\text{Cl}^-$	3.26
U(VI)	70.8 $\mu\text{M}$
Acetate	1.36
Citrate	73.0 $\mu\text{M}$



Results using standard data base

Results including formation constant for  $\text{Ca-UO}_2\text{-CO}_3$



# Samples for XAFS Analysis

- All samples 50  $\mu\text{M}$  U(VI) and 30mM  $\text{HCO}_3^-$ ,
- August 2002
  - Aug5000a: 5000  $\mu\text{M}$   $\text{CaCl}_2$ , 5mM acetate
  - Aug0a: 5mM acetate
  - Aug5000: 5000  $\mu\text{M}$   $\text{CaCl}_2$
- February 2003
  - Feb500: 500  $\mu\text{M}$   $\text{CaCl}_2$
  - Feb50: 50  $\mu\text{M}$   $\text{CaCl}_2$
  - Feb0:
- All samples kept anoxic during measurement



# Experimental Setup

- 50 $\mu$ M U Solution
  - $\Delta\mu = 6.5 \times 10^{-4} \text{ cm}^{-1}$
  - Sample thickness  $x = 3 \text{ mm}$
  - Absorption length  $\Delta\mu x = 2 \times 10^{-4}$
- MRCAT Beamline parameters
  - Using 13 element solid state detector
  - Incident x-ray intensity  $\sim 5 \times 10^{13} \text{ photons per second in a } 1 \text{ mm}^2 \text{ area at U L}_3\text{-edge}$
  - Fluorescent x-ray intensity  $\sim 100 \text{ photons per element per second above the edge}$
- XAFS scan parameters
  - One hour per scan (12 sec/pt) -> 1200 photons/(point element)
  - One scan  $\sim 4\%$  noise
  - 13 scans  $\sim 1\%$  noise
  - 4-6 scans per sample 0.5% noise
- 4-10 hours per sample



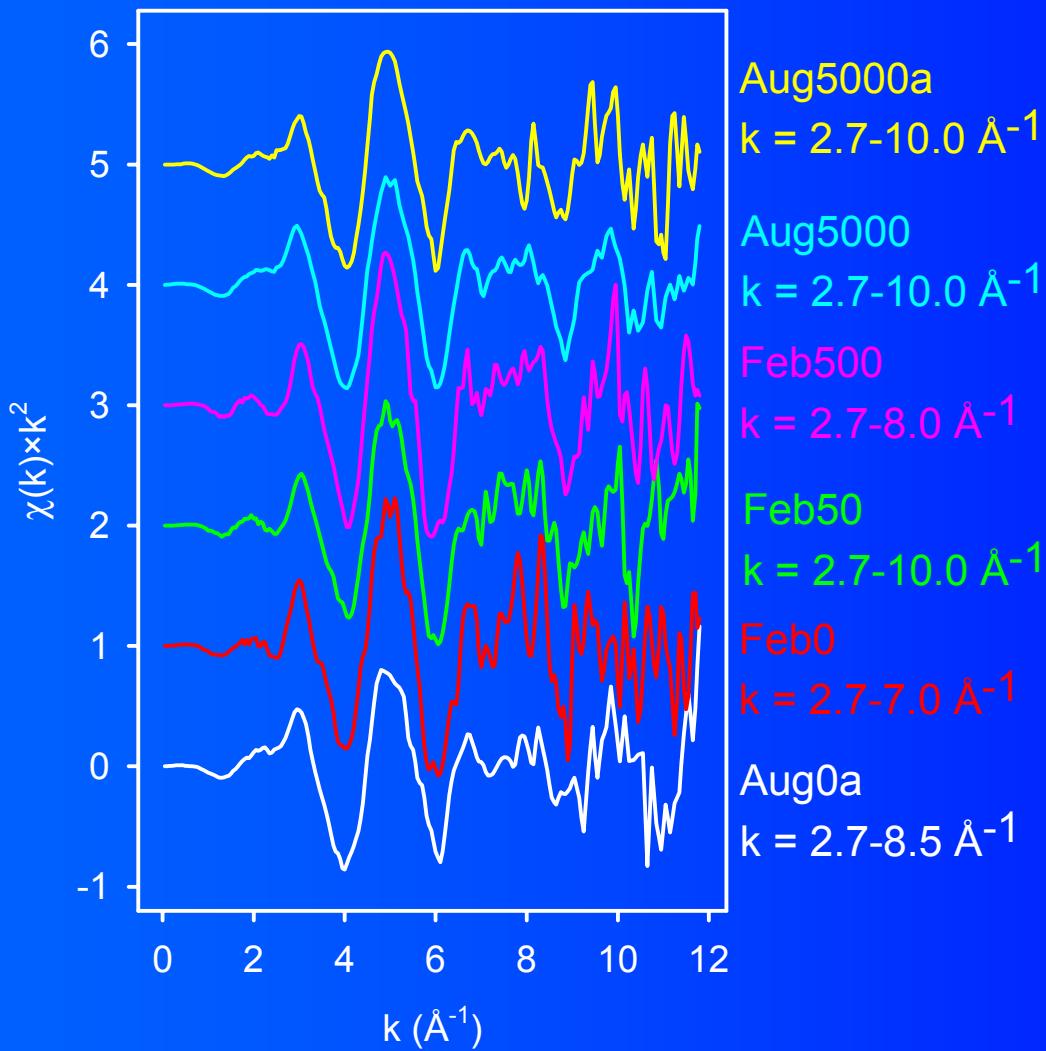
# Data collected with multielement detector, 1 hour/scan

Data	Number Of scans	RMS Noise %	Fluor step height*	Data range (Å <sup>-1</sup> )
Aug5000a	3	0.2	0.015	2.7-10.0
Aug0a	10	0.4	0.012	2.7-9.0
Aug5000	10	0.2	0.012	2.7-10.0
Feb500	8	0.2	0.005	2.7-10.0
Feb50	6	0.4	0.006	2.7-8.0
Feb0	4	0.4	0.007	2.7-7.0

\*detector gain, incident x-ray intensity and sample thickness similar from scan to scan



# EXAFS data

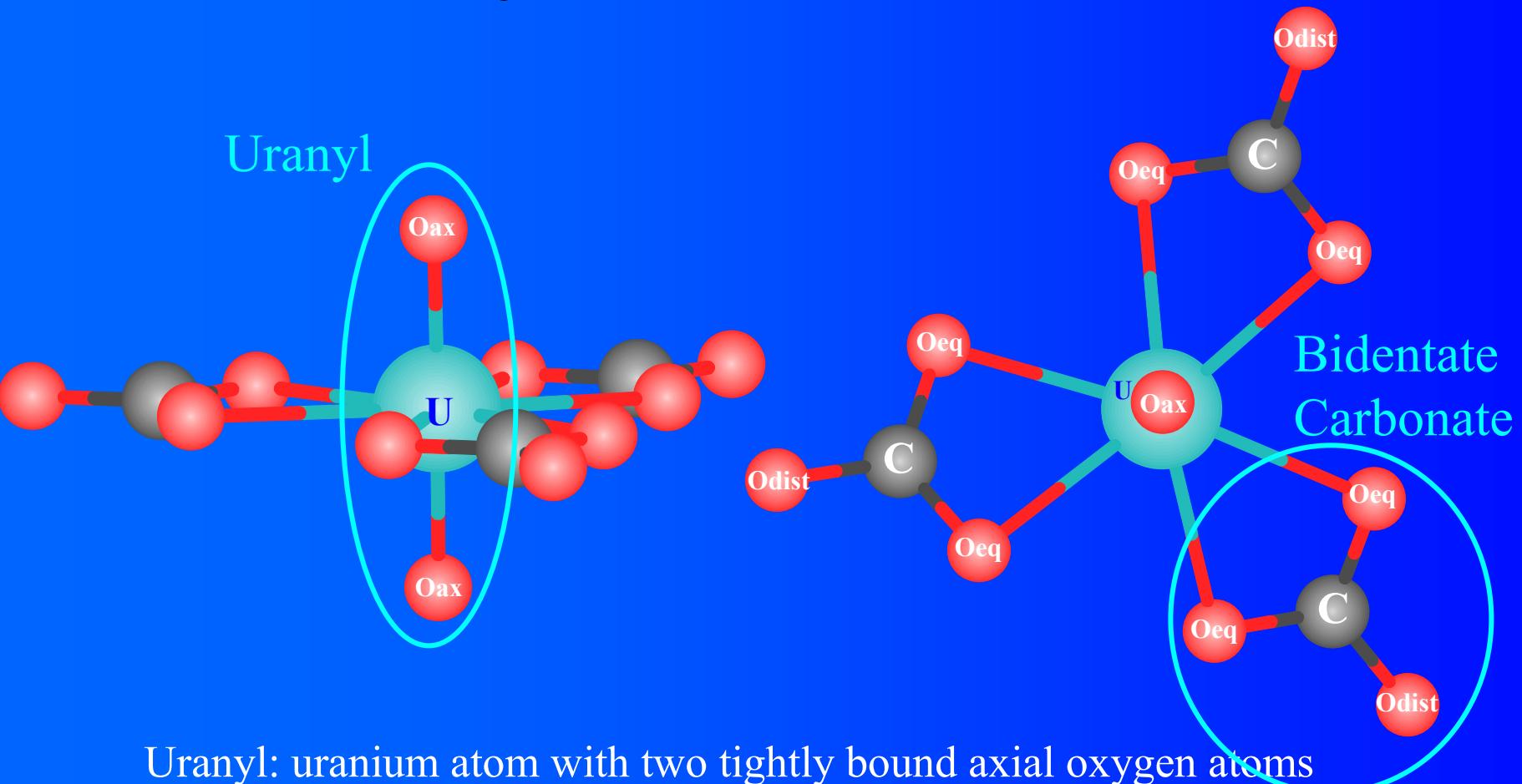


# EXAFS Modeling

- U-Ca-CO<sub>3</sub> structure
- Scattering paths of photoelectron
- EXAFS parameters
- Defining a fit region
- Multiple k-weight fit
- Multiple data set fit
- Results

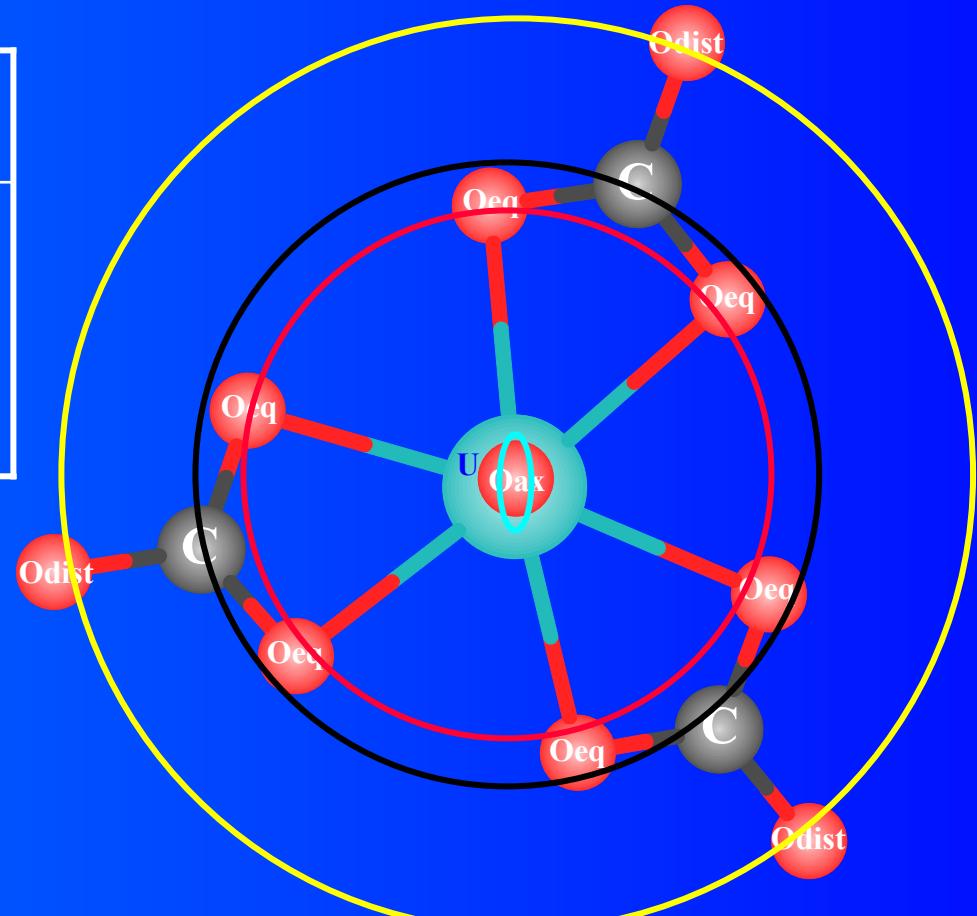


# Uranyl Carbonate structure



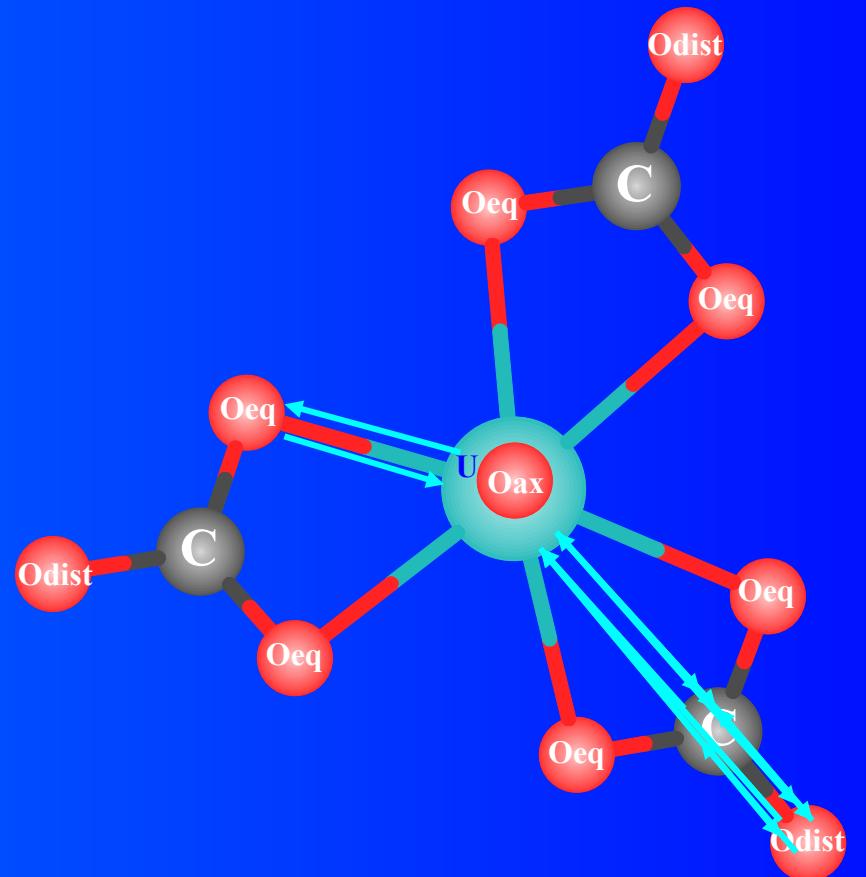
# Uranyl Carbonate scattering paths

Shells/Path	Number of paths	Distance (Å)
U→Oax	2	1.8
U→Oeq	6	2.4
U→C	3	2.9
U→Odist	3	4.2



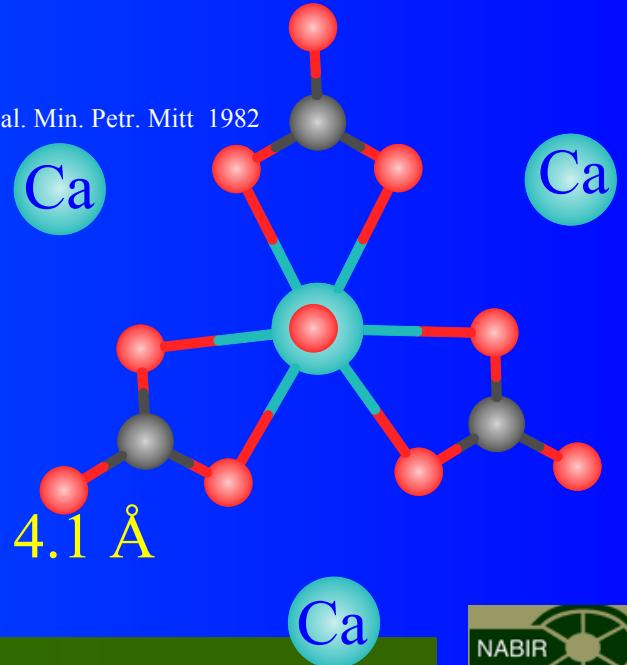
# Uranyl Carbonate scattering paths

Path	Number of paths	Distance (Å)
U→Oax	2	1.8
U→Oeq	6	2.4
U→Oax <sub>1</sub> →Oax <sub>2</sub>	2	3.6
U→Oax <sub>1</sub> →U→Oax <sub>2</sub>	2	3.6
U→Oax <sub>1</sub> →U→Oax <sub>1</sub>	2	3.6
U→C	3	2.9
U→Odist	3	4.2
U→C→Odist	6	4.2
U→C→Odist→C	3	4.2



# Where would you expect to find a Ca atom?

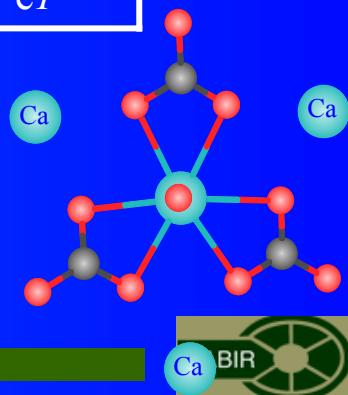
- U(VI) impurities in calcite ( $\text{CaCO}_3$ ) S. Kelly et al. ES&T 2002
  - ~6 Ca @ 3.78-4.01 Å
- U(VI) impurities in aragonite ( $\text{CaCO}_3$ ) R. Reeder et. al. ES&T 2000
  - ~6 Ca @ 3.8-4.75 Å
- Andersonite,  $\text{Na}_2\text{Ca}[\text{UO}_2(\text{CO}_3)_3] \cdot 5.6\text{H}_2\text{O}$  A. Coda et. al. Acta Crys. 1981
  - 2 Ca @ 3.96 Å
- Liebigite,  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$  K. Mereiter et. al. Min. Petr. Mitt 1982
  - 2 Ca @ 4.07 Å
- $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  aq Berhard, et al. Radiochim Acta 2001
  - Data consistent with 2 Ca at 3.94 Å



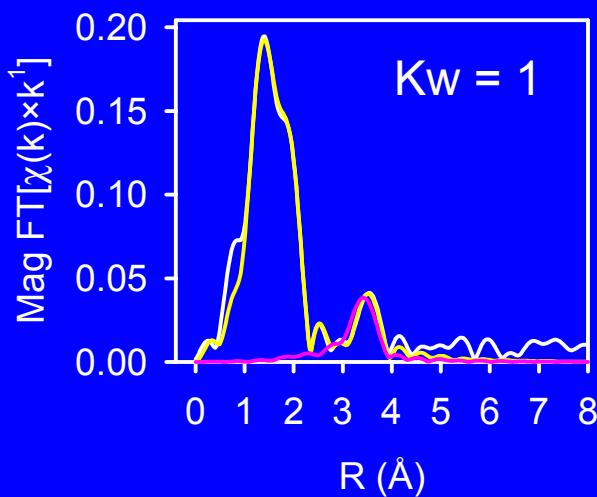
# U-Ca-CO<sub>3</sub> EXAFS parameters

Path	Number of paths	Distance (Å)	$\Delta r$	$\sigma^2$	$\Delta E$
U→Oax	2	1.8	$\Delta r_{oax}$	$\sigma^2_{oax}$	$\epsilon_{oax}$
U→Oeq	6	2.4	$\Delta r_{oeq}$	$\sigma^2_{oeq}$	$\epsilon_l$
U→Oax <sub>1</sub> →Oax <sub>2</sub>	2	3.6	2· $\Delta r_{oax}$	2· $\sigma^2_{oax}$	$\epsilon_{oax}$
U→Oax <sub>1</sub> →U→Oax <sub>2</sub>	2	3.6	2· $\Delta r_{oax}$	2· $\sigma^2_{oax}$	$\epsilon_{oax}$
U→Oax <sub>1</sub> →U→Oax <sub>1</sub>	2	3.6	2· $\Delta r_{oax}$	2· $\sigma^2_{oax}$	$\epsilon_{oax}$
U→C	3	2.9	$\Delta r_c$	$\sigma^2_c$	$\epsilon_l$
U→Odist	3	4.2	$\Delta r_{odist}$	$\sigma^2_{odist}$	$\epsilon_l$
U→C→Odist	6	4.2	$\Delta r_{odist}$	$\sigma^2_{odist}$	$\epsilon_l$
U→C→Odist→C	3	4.2	$\Delta r_{odist}$	$\sigma^2_{odist}$	$\epsilon_l$
U→Ca	Nca	3.8-4.1	$\Delta r_{ca}$	$\sigma^2_{ca}$	$\epsilon_l$

13 parameters  
 12-16 independent points/data set  
**Too many parameters!**

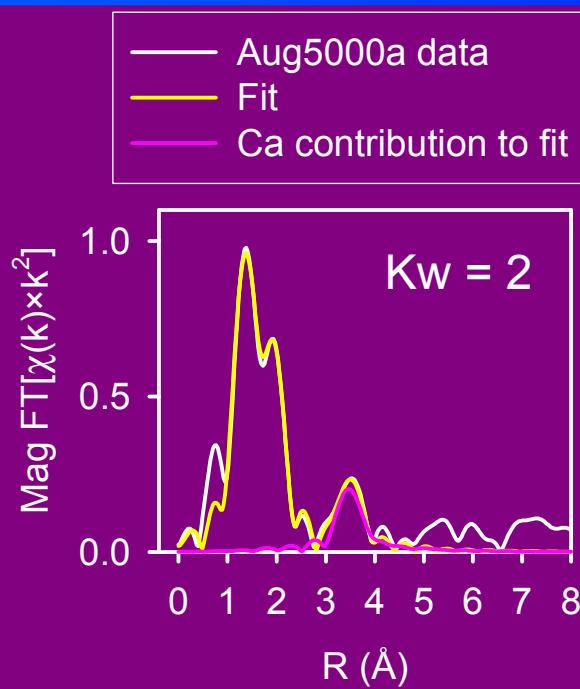


# Which k-weight and data range should we use?



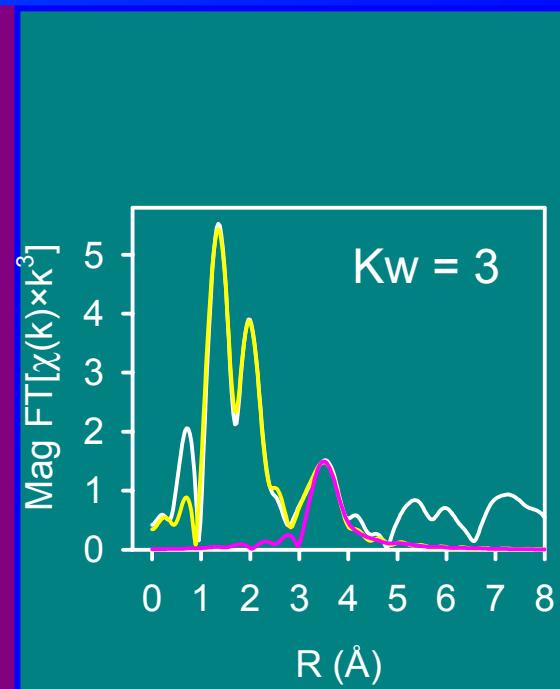
**Kw=1**

Path	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\times 10^{-3} \text{\AA}^{-2}$ )
U $\rightarrow$ Ca	$3.2 \pm$	$4.02 \pm$	$3 \pm$
	3.8	0.02	2
U $\rightarrow$ Odist	3	$4.10 \pm$	$20 \pm$
		0.15	10



**Kw=2**

Path	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\times 10^{-3} \text{\AA}^{-2}$ )
U $\rightarrow$ Ca	$2.3 \pm$	$4.02 \pm$	$2 \pm$
	4.7	0.02	11
U $\rightarrow$ Odist	3	$4.17 \pm$	$18 \pm$
		0.16	30

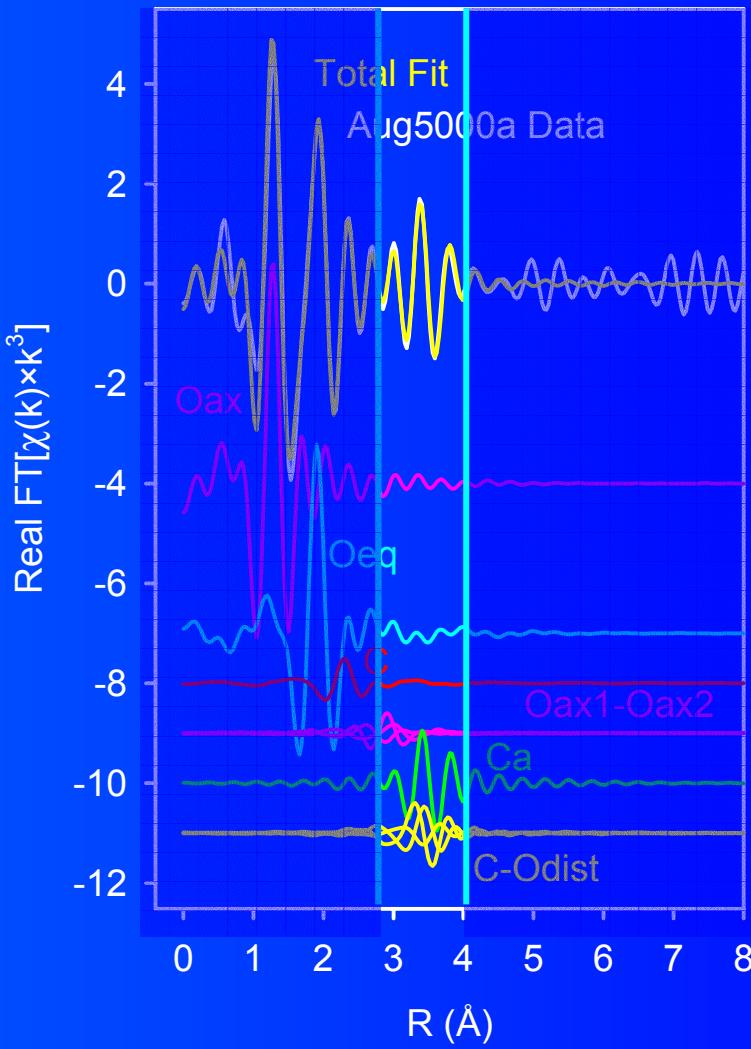
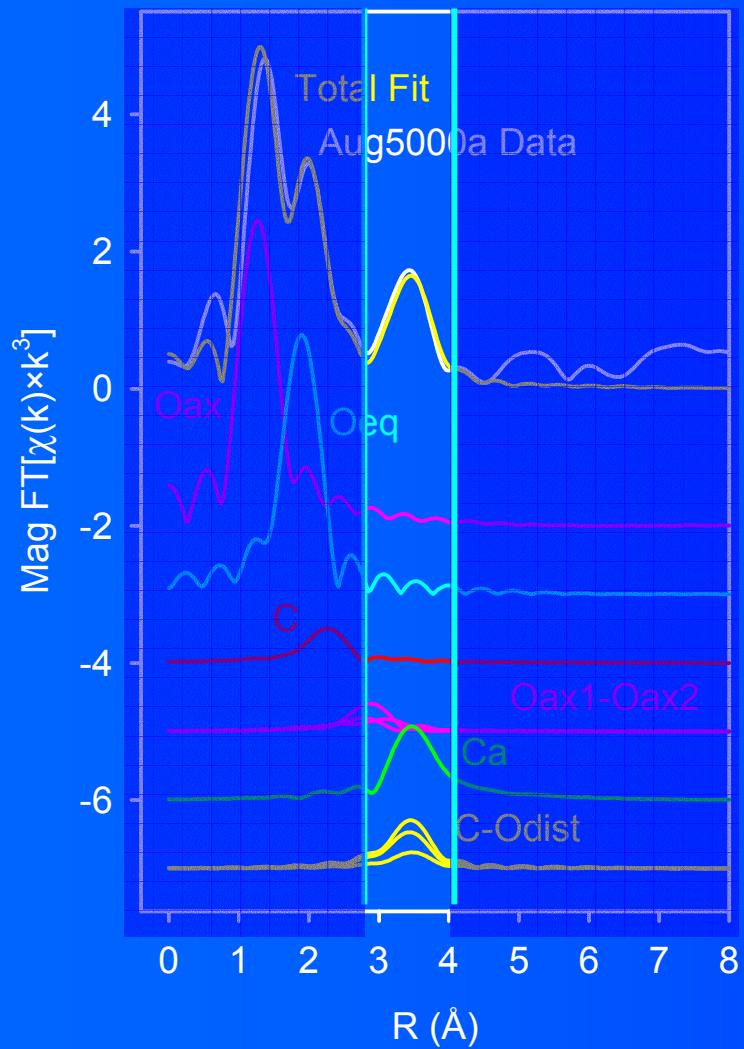


**Kw=3**

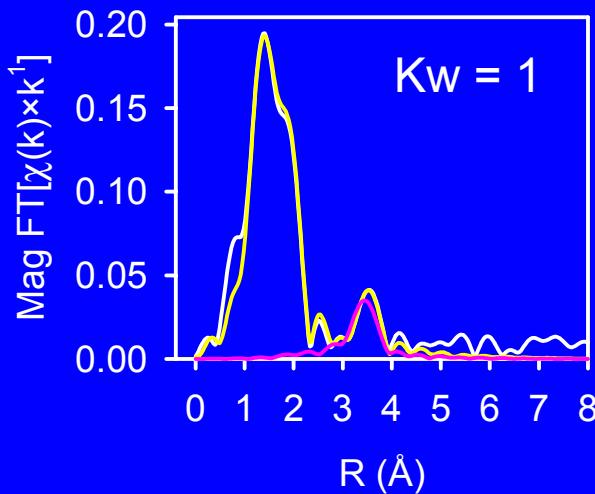
Path	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\times 10^{-3} \text{\AA}^{-2}$ )
U $\rightarrow$ Ca	$2.6 \pm$	$4.03 \pm$	$2 \pm$
	6.7	0.03	14
U $\rightarrow$ Odist	3	$4.19 \pm$	$22 \pm$
		0.25	6



# Path contributions to total Fit

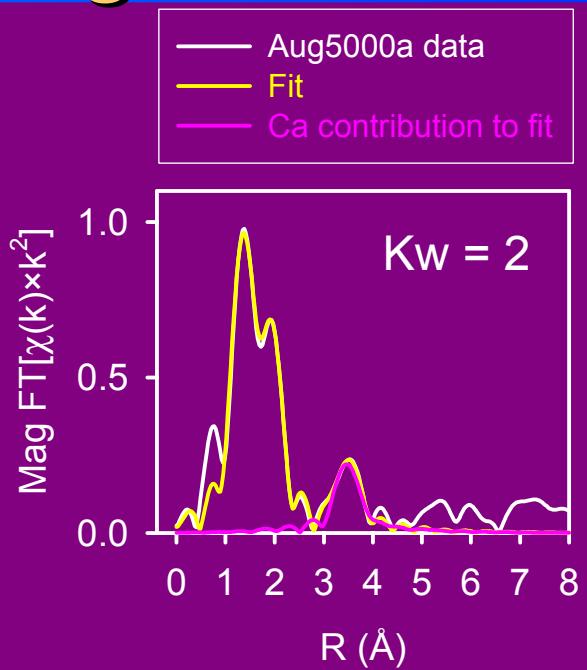


# Which k-weight should we use?



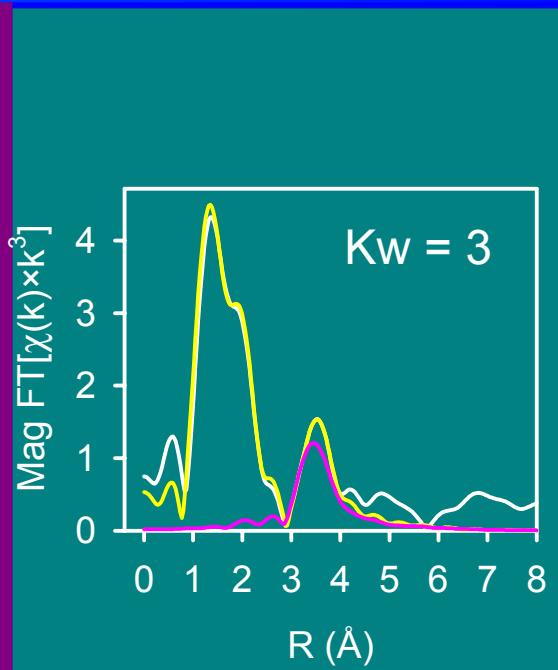
**Kw=1**

Path	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\times 10^{-3} \text{\AA}^{-2}$ )
U $\rightarrow$ Ca	$2.5 \pm$	$4.03 \pm$	$2 \pm$
	0.8	0.01	2
U $\rightarrow$ Odist	3	$4.16 \pm$	$21 \pm$
		0.02	2



**Kw=2**

Path	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\times 10^{-3} \text{\AA}^{-2}$ )
U $\rightarrow$ Ca	$2.3 \pm$	$4.02 \pm$	$1 \pm$
	1.1	0.05	3
U $\rightarrow$ Odist	3	$4.17 \pm$	$20 \pm$
		0.03	1



**Kw=3**

Path	N	R ( $\text{\AA}$ )	$\sigma^2$ ( $\times 10^{-3} \text{\AA}^{-2}$ )
U $\rightarrow$ Ca	$2.0 \pm$	$4.02 \pm$	$0 \pm$
	1.1	0.05	3
U $\rightarrow$ Odist	3	$4.18 \pm$	$19 \pm$
		0.03	1

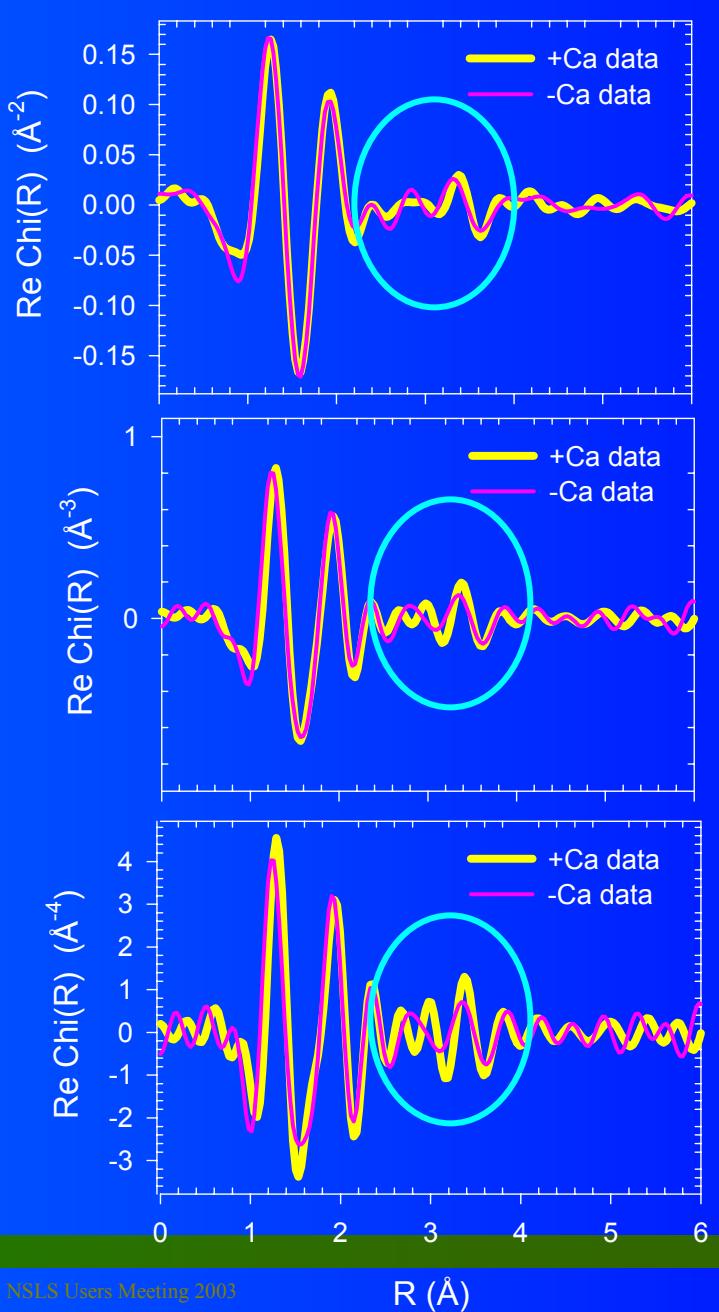
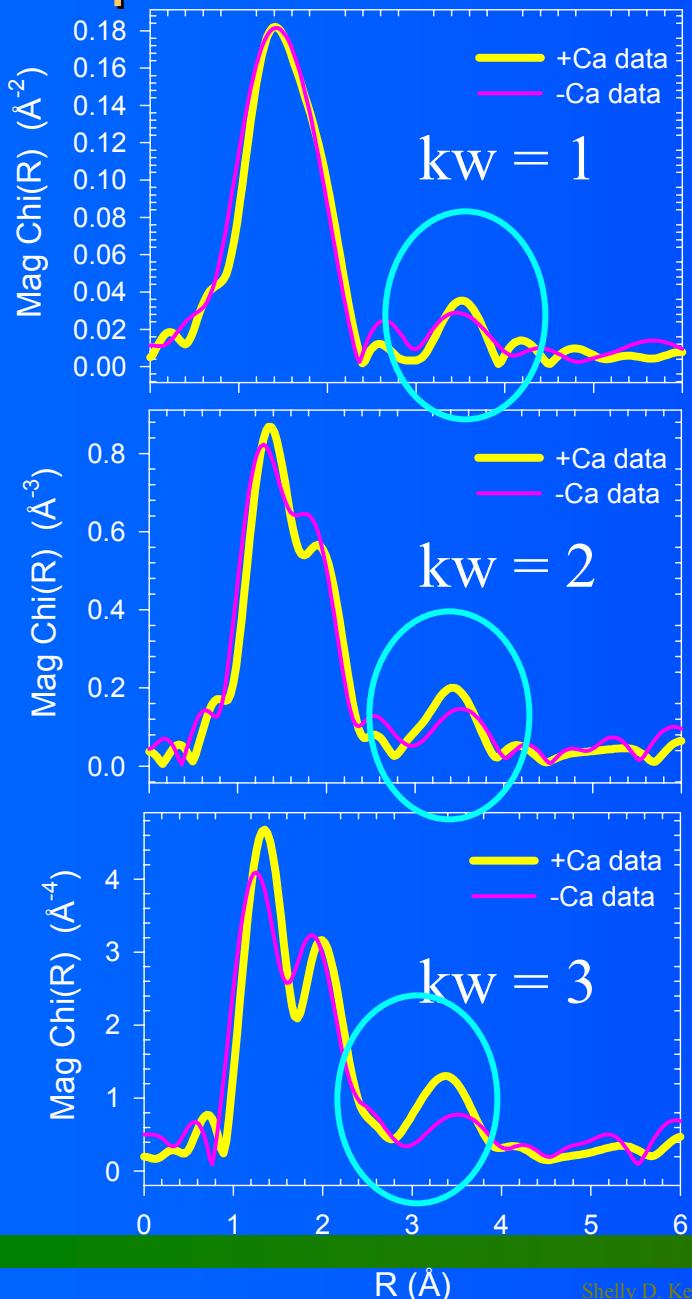


# k-dependence of XAFS signal

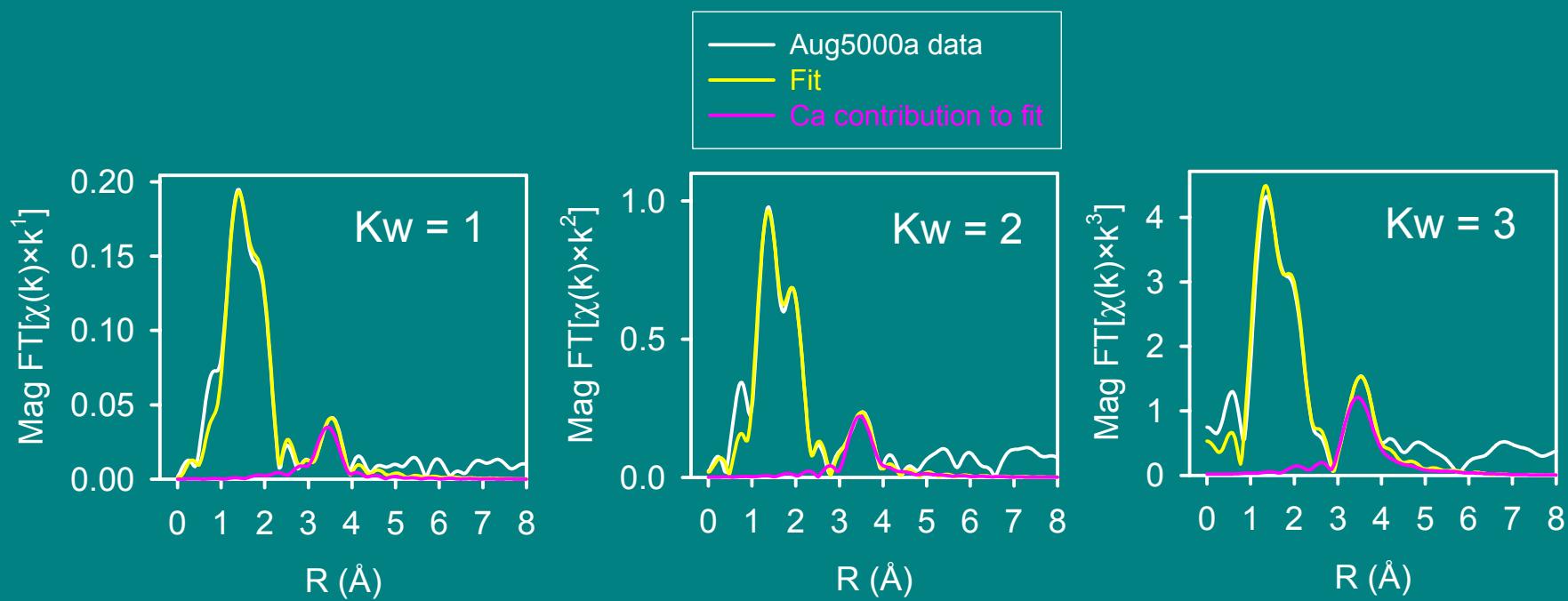
- Scattered photoelectron intensity depends on the number of electrons
  - O atom has 8 electrons
  - Ca atoms has 20 electrons
  - 2.5 O atoms = Ca atom in terms of electron density
- k-dependence of XAFS signal differs
- k-dependence is needed to distinguish between O<sub>dist</sub> and Ca



# k-dependence of Fourier Transform of XAFS data



# Simultaneous fit using $kw=1, 2$ , and $3$



Path	Number	Distance (Å)	$\sigma^2$ ( $\times 10^{-3}$ Å $^{-2}$ )
U→Ca	$2.5 \pm 0.8$	$4.03 \pm 0.01$	$2 \pm 2$
U→Odist	3	$4.16 \pm 0.02$	$21 \pm 2$



# Multiple data set fit

- Determine group parameters
- Fit entire data range 1.0 to 4.0 Å
- Fit Ca and Odist data region 2.9 to 4.0 Å
- Goals
  - To show Ca signal in all data were Ca has been added.
  - To determine the number of Ca atoms as U to Ca ratio varies.



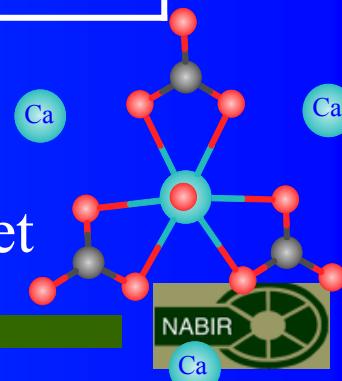
# EXAFS parameters For Multiple Data Set Fit

Path	Distance (Å)	Number of paths	$\Delta r$	$\sigma^2$	$\Delta E$
U→Oax	1.8	2	$\Delta r_{oax}$	$\sigma^2_{oax}$	$\epsilon_{oax}$
U→Oeq	2.4	6	$\Delta r_{oeq}$	$\sigma^2_{oeq}$	$\epsilon_l$
U→Oax <sub>1</sub> →Oax <sub>2</sub>	3.6	2	$2 \cdot \Delta r_{oax}$	$2 \cdot \sigma^2_{oax}$	$\epsilon_{oax}$
U→Oax <sub>1</sub> →U→Oax <sub>2</sub>	3.6	2	$2 \cdot \Delta r_{oax}$	$2 \cdot \sigma^2_{oax}$	$\epsilon_{oax}$
U→Oax <sub>1</sub> →U→Oax <sub>1</sub>	3.6	2	$2 \cdot \Delta r_{oax}$	$2 \cdot \sigma^2_{oax}$	$\epsilon_{oax}$
U→C	2.9	3	$\Delta r_c$	$\sigma^2_c$	$\epsilon_l$
U→Odist	4.2	3	$\Delta r_{odist}$	$\sigma^2_{odist}$	$\epsilon_l$
U→C→Odist	4.2	6	$\Delta r_{odist}$	$\sigma^2_{odist}$	$\epsilon_l$
U→C→Odist→C	4.2	3	$\Delta r_{odist}$	$\sigma^2_{odist}$	$\epsilon_l$
U→Ca	3.8-4.1	Nca	$\Delta r_{ca}$	$\sigma^2_{ca}$	$\epsilon_l$

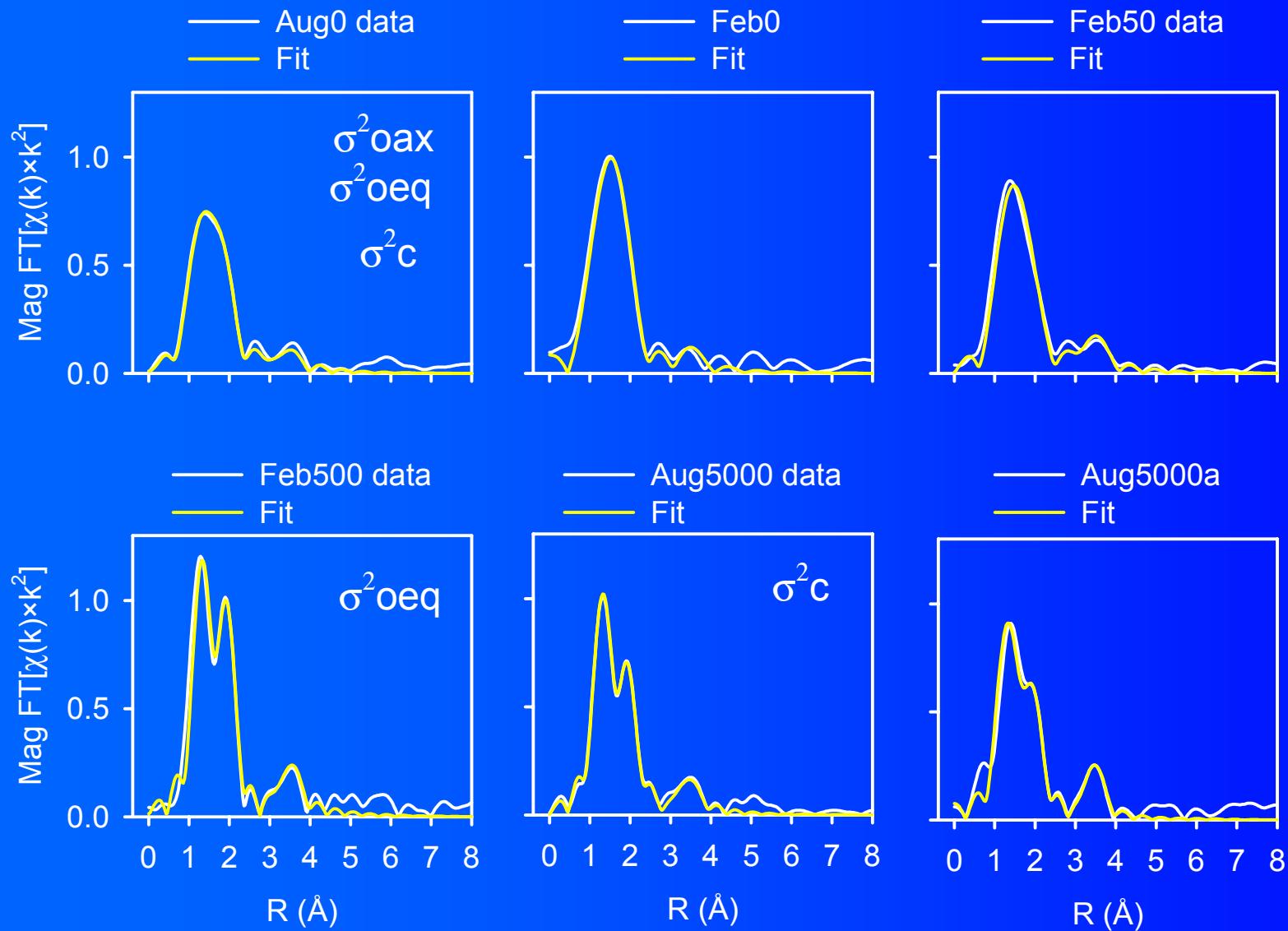
10 common + 3 parameters

10-17 independent points/data set

Fit all 6 data sets together ~ 5 parameters/data set



# XAFS Data and Fit



# Fit results for common parameters

Path	Number	Distance (Å)	$\sigma^2$ ( $\times 10^{-3}$ Å $^{-2}$ )
U→Oax	2	$1.79 \pm 0.01$	$1.5 \pm 1$
U→Oeq	6	$2.44 \pm 0.01$	$4.9 \pm 1$
U→C	3	$2.89 \pm 0.01$	$5.13 \pm 3$
U→Ca	x	$4.03 \pm 0.02$	$0 \pm 2$
U→Odist	3	$4.11 \pm 0.02$	$10 \pm 2$

# Fit results for specific parameters

Path	Aug0a	Feb0	Feb50	Feb500	Aug5000	Aug5000a
Nca	-	-	$1.4 \pm 0.6$	$1.3 \pm 0.8$	$0.8 \pm 0.4$	$1.6 \pm 0.6$
Eoax (eV)	$1.2 \pm 0.9$	$-0.7 \pm 0.9$	$0.3 \pm 0.9$	$0.8 \pm 1.2$	$2.0 \pm 0.8$	$-1.3 \pm 0.9$
Eoeq (eV)	$4.6 \pm 0.7$	$6.3 \pm 0.6$	$6.7 \pm 0.6$	$6.7 \pm 0.7$	$5.4 \pm 0.6$	$5.6 \pm 0.5$



Using entire Fit range R=1.0 to 4.0 Å  
 10 common + 3 parameters  
 10-17 independent points/data set

# EXAFS Parameters for Multiple Data Set Fit Only Ca Region

Path	Distance (Å)	Number of paths	$\Delta r$	$\sigma^2$	$\Delta E$
U→Oax	1.8	2	$\Delta r_{oax}$	$\sigma^2_{oax}$	$e_{oax}$
U→Oeq	2.4	6	$\Delta r_{oeq}$	$\sigma^2_{oeq}$	$e_I$
U→Oax <sub>1</sub> →Oax <sub>2</sub>	3.6	2	2· $\Delta r_{oax}$	2· $\sigma^2_{oax}$	$e_{oax}$
U→Oax <sub>1</sub> →U→Oax <sub>2</sub>	3.6	2	2· $\Delta r_{oax}$	2· $\sigma^2_{oax}$	$e_{oax}$
U→Oax <sub>1</sub> →U→Oax <sub>1</sub>	3.6	2	2· $\Delta r_{oax}$	2· $\sigma^2_{oax}$	$e_{oax}$
U→C	2.9	3	$\Delta r_c$	$\sigma^2_c$	$e_I$
U→Odist	4.2	3	$\Delta r_{odist}$	$\sigma^2_{odist}$	$e_I$
U→C→Odist	4.2	6	$\Delta r_{odist}$	$\sigma^2_{odist}$	$e_I$
U→C→Odist→C	4.2	3	$\Delta r_{odist}$	$\sigma^2_{odist}$	$e_I$
U→Ca	3.8-4.1	Nca	$\Delta r_{ca}$	$\sigma^2_{ca}$	$e_I$

Fit only Ca region R=2.9 to 4.0 Å  
 4 common + 1 parameters  
 5-8 independent points/data set  
 Fit all 6 data sets together ~ 2 parameters/data set



# Final Best-Fit Values

- Limited fit region R= 2.9 to 4.0 Å
- Results independent of k-weight (1,2, and 3) used in Fourier transform of data
- Multiple data sets used to optimize parameters that do not depended on Ca concentration

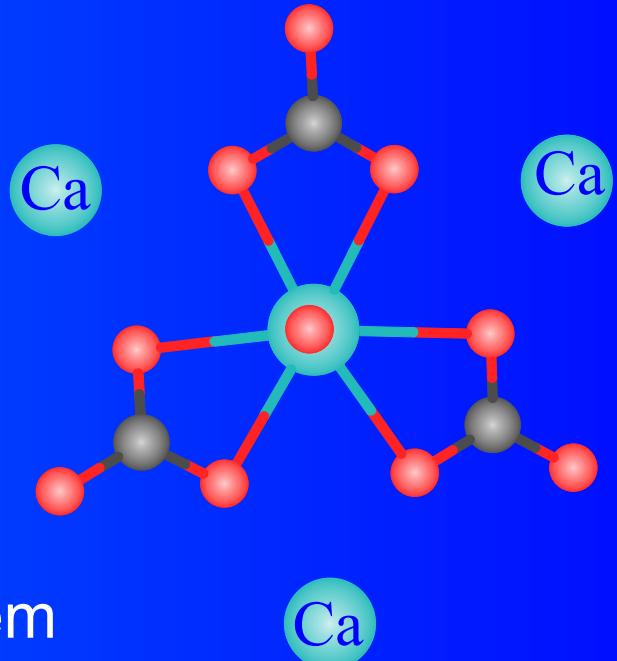
Path	Number	Distance (Å)	$\sigma^2$ ( $\times 10^{-3} \text{ \AA}^{-2}$ )
U→Ca	x	$4.03 \pm 0.01$	$0 \pm 2$
U→Odist	3	$4.10 \pm 0.10$	$10 \pm 4$

	Aug0a	Feb0	Feb50	Feb500	Aug5000	Aug5000a
<b>Nca</b>	-	-	<b><math>1.3 \pm 0.4</math></b>	<b><math>1.2 \pm 0.5</math></b>	<b><math>0.7 \pm 0.3</math></b>	<b><math>1.5 \pm 0.5</math></b>



# Conclusions

- Contributions to the XAFS signal used to model the data
  - 2 tightly bound axial oxygen
  - 6 equatorial oxygen (from carbonate)
  - 3 carbon atoms (from carbonate)
  - 3 oxygen atoms (from carbonate)
  - 0.4-2.0 Ca atoms
- Verification of a Ca-U(VI)-CO<sub>3</sub> complex in our experimental system by EXAFS
- Ca exerts a generic inhibition of bacterial U(VI) reduction



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